Diisopropylammonium 4-aminobenzenesulfonate

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The title molecular salt, $C_6H_{16}N^+ \cdot C_6H_6NO_3S^-$, was synthesized from a neutralization reaction between sulfanilic acid and diisopropylamine. The crystal structure consists of diisopropylammonium cations and 4-aminobenzene-sulfonate (sulfanilate) anions interacting through a series of N—H⋯O and C—H⋯O hydrogen bonds, leading to the formation of a three-dimensional network structure.

3D view
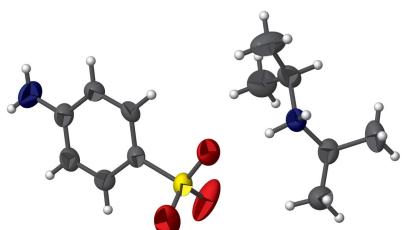
Chemical scheme
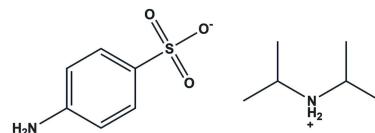
Structure description

Sulfanilates of alkylammonium cations, such as the sulfanilates of methylammonium (Schreuer, 1999), guanidinium (Russell *et al.*, 1994), triethylammonium (Li *et al.*, 2007) or tetramethylammonium (Wang *et al.*, 2016) have been reported. As a continuation of our work on alkylammonium salts (Sarr *et al.*, 2012), in order to study their interactions with metallic halides, we synthesized the title molecular salt from a neutralization reaction between sulfanilic acid, the structure of which has been reported by Low & Glidewell (2002), and diisopropylamine. Sulfanilic acid, a strong organic acid with pK_a = 3.23, donates its sulfonic proton to diisopropylamine to give the title organic salt, $C_6H_{16}N^+ \cdot C_6H_6NO_3S^-$. Its asymmetric unit comprises one diisopropylammonium cation and one sulfanilate anion (Fig. 1). The protonation of diisopropylamine leads to an irregular tetrahedral arrangement around the ammonium atom N2, as reported in related structures (Sarr *et al.*, 2012; Reiss & Meyer, 2011). The bond angles around this atom fall within normal ranges: 117.08 (18)° for angle C10—N2—C7, while the C—N—H2*N*/*M* angles are smaller and vary from 106.0 (13) to 109 (2) °. The arrangement around the sulfonate atom S1 is distorted tetrahedral, with the various O—S—C and O—S—O angles ranging between 106.82 (10)° for O1—S1—C1 to 112.51 (14)° for O2—S1—O1. In

Table 1
Hydrogen-bond geometry (Å, °).

| D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$M\cdots$O1	0.89 (2)	2.03 (2)	2.878 (3)	159 (2)
N2—H2$N\cdots$O1^i	0.88 (1)	2.11 (2)	2.922 (3)	152 (2)
N1—H1$M\cdots$O2^{ii}	0.84 (2)	2.21 (2)	3.013 (3)	160 (3)
N1—H1$N\cdots$O2^{iii}	0.84 (2)	2.57 (2)	3.316 (4)	149 (3)
N1—H1$N\cdots$O3^{iii}	0.84 (2)	2.67 (2)	3.441 (4)	153 (3)
C10—H10$\cdots$O3^{iv}	0.98	2.57	3.332 (3)	135
C12—H12$B\cdots$O3^i	0.96	2.58	3.468 (4)	155

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $x+1, y, z$; (iv) $x, y, z-1$.

the SO_3^- group the three S—-O distances are slightly different, *viz* S1—O2 = 1.4201 (18) Å, S1—O3 = 1.4325 (19) Å and S1—O1 1.4446 (17) Å, due to their different roles in hydrogen bonding.

In the crystal, the ions are connected through N—H$\cdots$O hydrogen bonds (Table 1). Atoms O1 and O2 of the sulfonate group are involved in rather strong N—H$\cdots$O hydrogen bonding. Atom O1 acts as an acceptor of two hydrogen bonds N2—H2$M\cdots$O1 and N2—H2$N\cdots$O1^i, forming a four-membered unit with inversion symmetry, enclosing an $R_4^2(8)$ ring motif (Table 1 and Fig. 2). These units are self-assembled through further N—H$\cdots$O hydrogen bonds involving atom
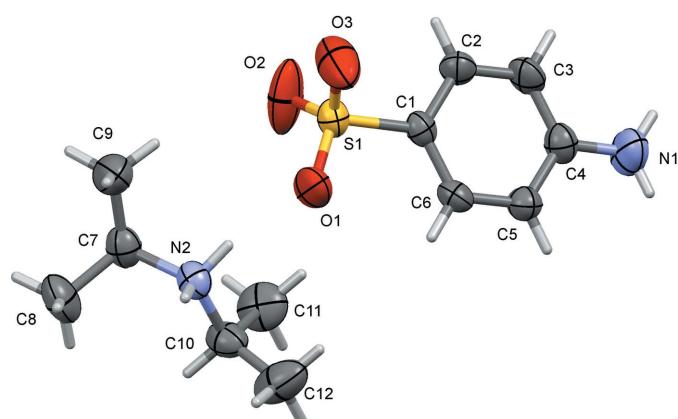
Figure 1
The structures of the molecular entities in the title salt. Displacement ellipsoids are drawn at the 50% probability level.
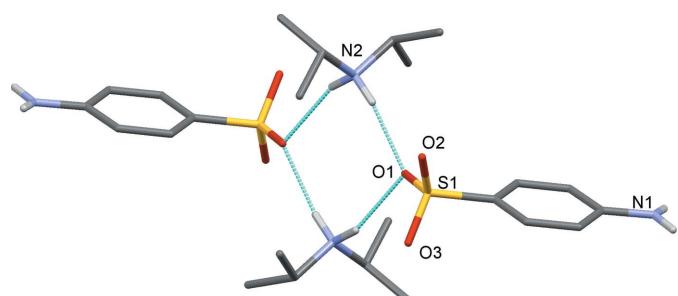

Figure 2
A view of the four-membered unit formed by N—H$\cdots$O hydrogen bonds (dashed lines; see Table 1), enclosing an $R_4^2(8)$ ring motif.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_{16}N^+ \cdot C_6H_6NO_3S^-$
M_r	274.38
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	296
a, b, c (Å)	8.1712 (4), 20.1515 (9), 9.1360 (4)
β (°)	105.806 (5)
V (Å^3)	1447.47 (11)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.23
Crystal size (mm)	$0.42 \times 0.26 \times 0.18$
Data collection	
Diffractometer	Agilent Xcalibur Sapphire2
Absorption correction	Analytical (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.952, 0.970
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6311, 2963, 2340
R_{int}	0.035
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.050, 0.136, 1.04
No. of reflections	2963
No. of parameters	179
No. of restraints	14
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.34, −0.28

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SIR92* (Altomare *et al.*, 1994), *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

O2 and the amino group of the sulfanilate anion (Fig. 3 and Table 1), forming a three-dimensional network. The hydrogen-bonded assembly is consolidated by a weak N1—H1$N\cdots$O3^{iii} hydrogen bond and two C—H$\cdots$O hydrogen bonds (Fig. 3 and Table 1), again involving atom O3.
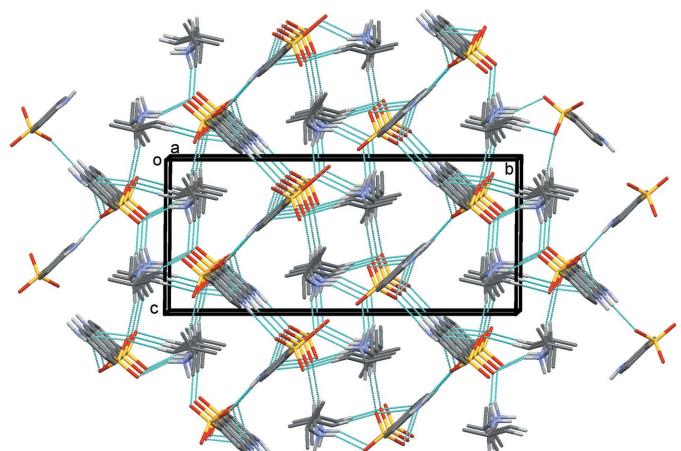
Figure 3
The crystal packing of the title molecular salt, viewed approximately along the *a* axis. Hydrogen bonds (see Table 1) are shown as dashed lines; for clarity, only H atoms involved in these interactions have been included.

Synthesis and crystallization

The title compound was obtained by addition of diisopropyl-amine (7.000 g, 0.069 mol) to an aqueous solution of sulfanilic acid (11.870 g, 0.068 mol) in an 1:1 ratio. The yellow solution obtained was stirred for one h and then filtered. Colourless plate-like crystals of the title molecular salt were obtained by slow evaporation of the filtrate after one week.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The N-bound H atoms were located in difference Fourier maps and refined with distance and angle restraints: N—H and H···H distances involving atom N1 are N—H = 0.86 (2) Å and H···H = 1.49 (2) Å, and for atom N2 are N—H = 0.90 (2) Å and H···H = 1.45 (2) Å, with $U_{iso}(H) = 1.2U_{eq}(N)$.

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full crystallographic data

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Crystal data
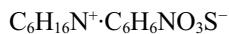
$C_6H_{16}N^+ \cdot C_6H_6NO_3S^-$	$F(000) = 592$
$M_r = 274.38$	$D_x = 1.259$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2619 reflections
$a = 8.1712$ (4) Å	$\theta = 3.8–27.1°$
$b = 20.1515$ (9) Å	$\mu = 0.23$ mm^{-1}
$c = 9.1360$ (4) Å	$T = 296$ K
$\beta = 105.806$ (5)°	Fragment of big plate, colourless
$V = 1447.47$ (11) Å^3	$0.42 \times 0.26 \times 0.18$ mm
$Z = 4$	

Data collection

Agilent Xcalibur Sapphire2 diffractometer	6311 measured reflections
Radiation source: Enhance (Mo) X-ray Source	2963 independent reflections
Graphite monochromator	2340 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3622 pixels mm^{-1}	$R_{int} = 0.035$
ω scans	$\theta_{max} = 26.4°$, $\theta_{min} = 3.6°$
Absorption correction: analytical (CrysAlis PRO; Agilent, 2014)	$h = -9 \rightarrow 10$
	$k = -24 \rightarrow 25$
$T_{min} = 0.952$, $T_{max} = 0.970$	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.050$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.136$	
$S = 1.04$	H atoms treated by a mixture of independent and constrained refinement
2963 reflections	
179 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 0.5536P]$ where $P = (F_o^2 + 2F_c^2)/3$
14 restraints	
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.34$ e Å^{-3}
	$\Delta\rho_{min} = -0.28$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.8387 (2)	0.15317 (10)	0.7706 (2)	0.0370 (4)
C2	0.8828 (3)	0.20191 (11)	0.8832 (2)	0.0462 (5)
H2	0.8014	0.2179	0.9284	0.055*
C3	1.0462 (3)	0.22647 (11)	0.9277 (3)	0.0527 (6)
H3	1.0738	0.259	1.0027	0.063*
C4	1.1704 (3)	0.20355 (11)	0.8624 (3)	0.0469 (5)
C5	1.1258 (3)	0.15426 (11)	0.7514 (2)	0.0448 (5)
H5	1.2074	0.1377	0.7073	0.054*
C6	0.9619 (3)	0.12987 (10)	0.7063 (2)	0.0415 (5)
H6	0.9342	0.0973	0.6315	0.05*
N1	1.3337 (3)	0.22806 (13)	0.9042 (3)	0.0775 (8)
S1	0.62887 (6)	0.12319 (3)	0.71455 (6)	0.04264 (19)
O1	0.6264 (2)	0.06898 (9)	0.6105 (2)	0.0681 (5)
O2	0.5214 (2)	0.17641 (10)	0.6456 (3)	0.1034 (9)
O3	0.5882 (3)	0.09977 (13)	0.8485 (2)	0.0992 (8)
H1M	1.362 (4)	0.2562 (15)	0.975 (3)	0.119*
H1N	1.405 (3)	0.2074 (16)	0.871 (4)	0.119*
C7	0.2667 (3)	0.09559 (11)	0.2422 (3)	0.0511 (6)
H7	0.2799	0.1423	0.2176	0.061*
C8	0.1624 (4)	0.06106 (14)	0.1017 (3)	0.0700 (8)
H8A	0.2188	0.0645	0.0225	0.105*
H8B	0.0524	0.0816	0.0687	0.105*
H8C	0.1494	0.0151	0.1241	0.105*
C9	0.1832 (4)	0.09238 (17)	0.3702 (3)	0.0785 (9)
H9A	0.1652	0.0468	0.3924	0.118*
H9B	0.0759	0.1151	0.3407	0.118*
H9C	0.2554	0.1132	0.459	0.118*
C10	0.5643 (3)	0.08053 (12)	0.2043 (3)	0.0547 (6)
H10	0.5049	0.0785	0.0957	0.066*
C11	0.6339 (4)	0.14973 (14)	0.2419 (4)	0.0739 (8)
H11A	0.6931	0.1523	0.348	0.111*
H11B	0.5419	0.181	0.2191	0.111*
H11C	0.711	0.1599	0.1823	0.111*
C12	0.7029 (4)	0.02934 (15)	0.2389 (4)	0.0865 (10)
H12A	0.7822	0.0387	0.1809	0.13*

H12B	0.6543	−0.0138	0.2123	0.13*
H12C	0.761	0.0305	0.3454	0.13*
N2	0.4402 (2)	0.06439 (9)	0.2941 (2)	0.0454 (4)
H2M	0.489 (2)	0.0764 (11)	0.3896 (18)	0.054*
H2N	0.423 (2)	0.0211 (7)	0.292 (3)	0.054*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0406 (10)	0.0316 (10)	0.0346 (10)	−0.0003 (8)	0.0031 (8)	0.0024 (8)
C2	0.0475 (12)	0.0402 (11)	0.0500 (12)	0.0032 (10)	0.0118 (10)	−0.0093 (9)
C3	0.0564 (13)	0.0411 (12)	0.0551 (13)	−0.0046 (10)	0.0059 (11)	−0.0181 (10)
C4	0.0448 (12)	0.0404 (11)	0.0509 (12)	−0.0049 (10)	0.0051 (10)	−0.0006 (10)
C5	0.0447 (12)	0.0476 (12)	0.0432 (11)	−0.0021 (10)	0.0140 (9)	−0.0033 (9)
C6	0.0503 (12)	0.0410 (11)	0.0324 (10)	−0.0051 (9)	0.0100 (9)	−0.0061 (8)
N1	0.0490 (13)	0.0770 (18)	0.103 (2)	−0.0183 (12)	0.0153 (13)	−0.0326 (14)
S1	0.0397 (3)	0.0396 (3)	0.0442 (3)	−0.0028 (2)	0.0039 (2)	0.0011 (2)
O1	0.0552 (10)	0.0690 (12)	0.0768 (12)	−0.0175 (9)	0.0123 (9)	−0.0323 (10)
O2	0.0505 (11)	0.0571 (12)	0.173 (2)	0.0051 (9)	−0.0205 (13)	0.0298 (14)
O3	0.0780 (14)	0.162 (2)	0.0608 (12)	−0.0538 (15)	0.0235 (10)	0.0010 (14)
C7	0.0507 (13)	0.0405 (12)	0.0561 (13)	−0.0019 (10)	0.0041 (10)	−0.0012 (10)
C8	0.0728 (17)	0.0691 (17)	0.0521 (14)	−0.0021 (14)	−0.0102 (12)	0.0000 (13)
C9	0.0555 (16)	0.109 (2)	0.0722 (18)	−0.0051 (16)	0.0195 (13)	−0.0246 (18)
C10	0.0621 (14)	0.0582 (14)	0.0486 (13)	−0.0153 (12)	0.0231 (11)	−0.0065 (11)
C11	0.085 (2)	0.0542 (16)	0.090 (2)	−0.0174 (15)	0.0366 (17)	0.0077 (14)
C12	0.078 (2)	0.0658 (19)	0.134 (3)	−0.0093 (16)	0.060 (2)	−0.0197 (19)
N2	0.0478 (10)	0.0454 (10)	0.0415 (9)	−0.0075 (9)	0.0096 (8)	0.0018 (8)

Geometric parameters (Å, º)

C1—C6	1.379 (3)	C7—H7	0.98
C1—C2	1.396 (3)	C8—H8A	0.96
C1—S1	1.758 (2)	C8—H8B	0.96
C2—C3	1.377 (3)	C8—H8C	0.96
C2—H2	0.93	C9—H9A	0.96
C3—C4	1.389 (3)	C9—H9B	0.96
C3—H3	0.93	C9—H9C	0.96
C4—N1	1.376 (3)	C10—C12	1.501 (4)
C4—C5	1.395 (3)	C10—N2	1.503 (3)
C5—C6	1.380 (3)	C10—C11	1.510 (3)
C5—H5	0.93	C10—H10	0.98
C6—H6	0.93	C11—H11A	0.96
N1—H1M	0.841 (17)	C11—H11B	0.96
N1—H1N	0.839 (17)	C11—H11C	0.96
S1—O2	1.4201 (18)	C12—H12A	0.96
S1—O3	1.4325 (19)	C12—H12B	0.96
S1—O1	1.4446 (17)	C12—H12C	0.96
C7—C8	1.504 (3)	N2—H2M	0.888 (15)

C7—N2	1.505 (3)	N2—H2N	0.884 (14)
C7—C9	1.507 (4)		
C6—C1—C2	118.81 (19)	H8A—C8—H8B	109.5
C6—C1—S1	121.74 (15)	C7—C8—H8C	109.5
C2—C1—S1	119.45 (16)	H8A—C8—H8C	109.5
C3—C2—C1	120.3 (2)	H8B—C8—H8C	109.5
C3—C2—H2	119.9	C7—C9—H9A	109.5
C1—C2—H2	119.9	C7—C9—H9B	109.5
C2—C3—C4	121.1 (2)	H9A—C9—H9B	109.5
C2—C3—H3	119.4	C7—C9—H9C	109.5
C4—C3—H3	119.4	H9A—C9—H9C	109.5
N1—C4—C3	121.9 (2)	H9B—C9—H9C	109.5
N1—C4—C5	119.9 (2)	C12—C10—N2	108.6 (2)
C3—C4—C5	118.1 (2)	C12—C10—C11	111.8 (2)
C6—C5—C4	120.7 (2)	N2—C10—C11	110.13 (19)
C6—C5—H5	119.6	C12—C10—H10	108.7
C4—C5—H5	119.6	N2—C10—H10	108.7
C1—C6—C5	120.85 (19)	C11—C10—H10	108.7
C1—C6—H6	119.6	C10—C11—H11A	109.5
C5—C6—H6	119.6	C10—C11—H11B	109.5
C4—N1—H1M	120 (2)	H11A—C11—H11B	109.5
C4—N1—H1N	116 (2)	C10—C11—H11C	109.5
H1M—N1—H1N	123 (3)	H11A—C11—H11C	109.5
O2—S1—O3	111.62 (17)	H11B—C11—H11C	109.5
O2—S1—O1	112.51 (14)	C10—C12—H12A	109.5
O3—S1—O1	110.36 (13)	C10—C12—H12B	109.5
O2—S1—C1	107.83 (10)	H12A—C12—H12B	109.5
O3—S1—C1	107.42 (10)	C10—C12—H12C	109.5
O1—S1—C1	106.82 (10)	H12A—C12—H12C	109.5
C8—C7—N2	110.0 (2)	H12B—C12—H12C	109.5
C8—C7—C9	111.8 (2)	C10—N2—C7	117.08 (18)
N2—C7—C9	108.9 (2)	C10—N2—H2M	107.0 (13)
C8—C7—H7	108.7	C7—N2—H2M	108.9 (13)
N2—C7—H7	108.7	C10—N2—H2N	109.0 (13)
C9—C7—H7	108.7	C7—N2—H2N	106.0 (13)
C7—C8—H8A	109.5	H2M—N2—H2N	109 (2)
C7—C8—H8B	109.5		

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2M⋯O1	0.89 (2)	2.03 (2)	2.878 (3)	159 (2)
N2—H2N⋯O1[i]	0.88 (1)	2.11 (2)	2.922 (3)	152 (2)
N1—H1M⋯O2[ii]	0.84 (2)	2.21 (2)	3.013 (3)	160 (3)
N1—H1N⋯O2[iii]	0.84 (2)	2.57 (2)	3.316 (4)	149 (3)
N1—H1N⋯O3[iii]	0.84 (2)	2.67 (2)	3.441 (4)	153 (3)

C10—H10···O3[iv]	0.98	2.57	3.332 (3)	135
C12—H12B···O3[i]	0.96	2.58	3.468 (4)	155

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x+1, -y+1/2, z+1/2$; (iii) $x+1, y, z$; (iv) $x, y, z-1$.